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FINAL REPORT

THE DESIGN AND MONITORING OF A MODIFIED URANIUM BIOSORPTION PILOT PLANT

BY

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37 pp

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EXECUTIVE SUMMARY

Inactive microbial biomass of the type Rhizopus arrhizus was immobilized in particulate form using the proprietary technology that has been developed by Dr. Marios Tsezos, at McMaster University in Hamilton, Ontario, Canada. Two continuous upflow packed bed reactors (R1 and R2) with a two stage feed solution pretreatment were designed, constructed and charged with the immobilized biomass. Each column was 45 inches long, had an inside diameter of 2.5 inches and was charged with about 2 lb of immobilized biomass. Reactor one was charged with the same immobilized biomass that was used for 14 months continuously in previous similar pilot plant experiments. Reactor 2 was charged with fresh immobilized biomass.

The column feed was pH=4, settled, biological leachate supplied by Denison Mines from their Elliot Lake uranium biological leaching works with an average initial uranium concentration of about 140 mg/L. The pilot plant was designed to continuously extract the uranium from the biological leachate and to recover it in the form of a concentrated eluate. The pilot plant was operated for about 12 months intermittently. To date, these experiments have been the largest pilot plant using immobilized microbial biomass for the selective extraction and recovery of a chemical compound. Up to 55 fold concentration of the uranium was achieved using sodium bicarbonate as the eluant. Uranium concentrations as high as 7.8 g/l were reached in the eluates.

The behaviour of other elements present in the bioleach solutions were also examined. Each element presented specific loading and elution characteristics and the biosorption of uranium from bioleach solutions constituted a complex system. The selectivity of the process for uranium was conclusively demonstrated, as well as the possibility of using the immobilized biomass to separate aluminum, yttrium and rare

earths from uranium and thorium. A hypothesis on the influence of iron, aluminum and thorium on uranium biosorption was advanced further.

The implemented pretreatment of the pilot plant feed, however, was such that it allowed the gradual accumulation of competing ions in the active biomass regions thus gradually reducing the average uranium capacity of the immobilized biomass packed bed in the first few cycles. This project also demonstrated conclusively the ability of the immobilized biomass particles to operate over long periods of continuous industrial type use. The kinetic properties of the immobilized biomass particles remained robust over that period of time. Appropriate feed solution pretreatment should provide the answer to the uptake capacity problems observed. This technology, characterised by high selectivity, can be used not only to remove and/or recover uranium from dilute complex wastewaters or industrial solutions but also as a specific separation/recovery technology for metals, like uranium, thorium, yttrium and aluminum and for the treatment of radioactive waste waters and polluted ground water.

SOMMAIRE

De la biomasse microbiale inactive de type Rhizopus arrhizus a été immobilisée sous forme solide grace à une nouvelle technique développée par Mario Tsesos à McMaster University, Hamilton, Ontario, Canada. Deux réacteurs à écoulement vertical avec prétraitement en deux étapes de la solution nourricière ont été conçus et remplis avec de la biomasse immobilisée. Chaque réacteur, d'une longueur de 45 pouces et de diamètre intérieur de 2.5 pouces, ont été remplis avec environ 2 livres de biomasse accumulée. Le réacteur 1 a été rempli avec la même biomasse immobilisée qui fut utilisée de façon continue pendant 14 mois lors d'essais précédents. Le réacteur 2, quant à lui a été rempli avec de la biomasse fraîche.

La solution nourricière (ph=4) est une solution de lessivage biologique fournie par les mines Denison et provenant de leur usine de lessivage biologique à Elliot Lake. La concentration initiale en uranium de cette solution était environ de 140 mg/l. Le projet pilote fut conçu de façon à ce que l'uranium soit extrait de façon continue et récupéré par élution dans une solution concentrée. Le projet pilote fut opéré de façon intermittente pendant 12 mois, ce qui en fait la plus importante expérience d'extraction sélective d'un composé chimique réalisée jusqu'à maintenant. L'uranium a été concentré par un facteur de 55 en utilisant du bicarbonate de soude dans le processus d'élution. Des concentrations jusqu'à 7.8 g/l furent atteintes dans les solution d'élution.

Le comportement des autres éléments présents dans la solution de lessivage biologique a aussi été examiné. Les concentrations et caracteristiques d'élution sont specifiques à chaque élément démontrant ainsi que le processus de biosorption de l'uranium à partir d'une solution de lessivage biologique est un système complexe. La sélectivité du processus pour l'uranium est démontré de façon concluante ainsi que la possibilité d'utiliser de la biomasse immobilisée pour séparer les éléments aluminium, yttrium et les terres rares de l'uranium et du thorium. L'influence du fer, de l'aluminium et du thorium sur la

biosorption de l'uranium est aussi discutée.

Le processus de prétraitement pour la solution nourricière est tel qu'il permet l'accumulation d'ions compétiteurs dans la biomasse active, ainsi réduisant sa capacité d'absorption de l'uranium. Le projet a aussi démontré de façon concluante la capacité des particules de biomasse immobilisée à opérer durant de longues périodes de temps. Les propriétés cinétiques de la biomasse immobilisée sont restées à peu près constantes durant cette période de temps. L'utilisation de solutions nourricières appropriées durant le prétraitement devrait donner une réponse au problème de la capacité d'absorption observée. Cette technologie, caracterisée par une grande sélectivité, peut être utilisée pour enlever ou récupérer l'uranium à partir de solutions complexes diluées et aussi en tant que processus de séparation/récupération pour des métaux tels que: uranium, thorium, yttrium et aluminium et, finalement, pour le traitement d'eaux usées ou nappes phréatiques polluées.

THE DESIGN AND MONITORING OF A MODIFIED URANIUM BIOSORPTION CONTINUOUS PILOT PLANT

1. INTRODUCTION

1.1 Project Scope and Objectives

Denison Mines, in co-operation with the Department of Energy, Mines and Resources, is conducting in situ commercial bioleaching of uranium ore underground. The volumes of leachate encountered in bioleaching are, understandably, large and low in uranium concentration. Furthermore several cases of fresh water aquifers polluted by radioactive or non radioactive ions have been identified. In the case of uranium bioleaching the cost of pumping millions of gallons per day of such dilute waters to the surface for conventional uranium extraction, is high and it is desired to devise a better process to selectively and efficiently recover uranium from these dilute solutions. In the case of ground water pollution a selective low cost and efficient process for removing radionuclides from ground water is not available yet.

In the past ten years, a proprietary process for the selective extraction of ions from dilute complex solutions using immobilized microbial biomass has been developed at McMaster University by Dr. M. Tsezos. In 1989, a continuous pilot plant using immobilized *Rhizopus arrhizus* biomass in an upflow column was operated for 14 months on industrial biologically leached uranium solutions. This pilot plant yielded uranium eluate peak concentrations corresponding to a 30-fold concentration of the initial uranium present in the Denison Mines bioleach solutions that contained 300 mg U/l. A reduction of the uranium biosorption capacity of the immobilized biomass during the first three cycles of operation was observed and the causes were identified. Following these encouraging results, additional immobilized biomass was

produced at McMaster University by Dr. M. Tsezos and it was decided to operate a larger pilot plant, with feed pretreatment, to test further this new technology. The present project focusses on the operation of this larger pilot plant. The main objectives of the present contract are as follows:

1. Using his experience and detailed mechanistic understanding of uranium biosorption Dr M. Tsezos will develop and design a new modified conceptual flow sheet for the continuous biosorptive recovery of uranium from Elliot Lake biological leachates.

2. The individual unit operations involved in the new flow sheet will be sized and the detailed design of the new proposed flow sheet will be given to CANMET for construction of the components. A complete sampling and operating protocol will be provided for the new pilot plant.

3. Dr. M. Tsezos in collaboration with CANMET will supervise the construction of the new pilot plant.

4. Upon completion, the pilot plant will be tested hydraulically and debugged.

5. The debugged pilot plant will be charged with immobilized microbial biomass and the first uranium biosorption/elution cycle will be carried out.

6. The subsequent pilot plant performance will be monitored in collaboration with CANMET personnel and a performance review will be carried out once every month.

7. Upon completion of the pilot plant experiments Dr. M. Tsezos will compare the pilot plant performance to previous experience and write a final report.

The uranium biosorption pilot plant will be located at CANMET's Biotechnology section premises that are suitable for such larger scale work. The pilot plant would operate during the uranium loading part of the cycle (beginning of the cycle) with pH=4 settled bioleach solution, in a packed bed upflow mode at a fixed flow rate charged with the same type of immobilised biomass that has been used by Dr. M. Tsezos in the previous pilot plant.

The pilot plant will have provisions to wash the immobilised biomass at the end of the loading cycle with a fixed volume of water. Then the reactors would be switched to the uranium elution mode by passing through a fixed volume of sodium bicarbonate eluant at a Solid to Liquid ratio of about 20:1 mg/mL. After elution the biomass beds will be washed again with water and revert again to the beginning of a new uranium recovery cycle.

The present contract (DSS 23440-0-9055/01-SQ) was conducted on behalf of the Biotechnology Section of CANMET. The designated CANMET scientific authority was Dr. R. G. L. McCready.

2. MATERIALS AND METHODS

2.1 Biosorbent Production

The biosorbent was produced by Dr. M. Tsezos at McMaster University. A strain of R. arrhizus was grown in a twin 14-L bench top fermentor in a nutrient broth under carefully controlled conditions. Sterile conditions were used to

prevent contamination by the microorganisms. The R. arrhizus was separated from the nutrient solution by filtration, was washed thoroughly and autoclaved. The biomass was then freeze-dried. The dried biomass was size classified and immobilized using a proprietary immobilization process to produce particles of 20-25 mesh size. Several batches of biomass were produced and tested to compare the uranium uptake between batches. The uranium uptake of the biomass batches was examined before and after immobilization and was found to be consistent.

2.2 Bioleach Solution Processing

The mine process water used in this work was bioleach solutions from the Denison Mines underground bacterial leaching stopes in Elliot Lake, Ontario received in 200-litre drums with an initial pH of about 2.4. The bioleach solution was adjusted close to a pH 4.0 with concentrated NaOH in large 200-litre polymeric feed tanks and was allowed to settle. It has been shown in literature that pH 4.0 is the optimum pH for uranium biosorption. The range of concentrations observed for the most significant elements in the received bioleach solution and the corresponding processed bioleach solution concentrations have been discussed in detail in our previous report. The pH of the processed bioleach solutions was in the range 3.7-4.0.

Generally, at least 85% of Th precipitated during adjustment of solution to pH 4, and between 98% and 99.9% of Fe precipitated at the same time. Uranium loss due to pH adjustment was between 0% and 10%. Part of Al, Si and Y also precipitated.

2.3 Pilot Plant Characteristics and Operation

The new pilot plant design incorporates a two stage

physical pretreatment of the feed solution. The first pretreatment step (PA) consists of an upflow deep bed sand filter with a diameter of 6.4 cm and sand depth of 100 cm. The second pretreatment step (PB) consists of a second similar column charged with glass wool. Following reactor PB is the first biomass reactor (R1) which is charged with the same biomass that had been used for over one year in the previous pilot plant uranium recovery experiments. In series to R1 is the second biomass reactor R2 which is charged with fresh immobilized bioimass.

The R1 and R2 columns used in the pilot plant were 6.4 cm i.d. and 120 cm long transparent acrylic cylinders. The columns were loaded with ca. 1 kg of biomaterial each. The biomaterial was washed with tap water for 60 hours at 6.5 ml/min prior to the first loading with pH 4 bioleach solution. Figure 1 presents a schematic diagram of the pilot plant. The biomaterial in the columns was contacted with the pH 4 settled bioleach solution in an up flow direction. The feed solution was passed through a tangential flow filter prior to PA. The average flow rate was 32.0 mL/min (Standard deviation: 2 mL/min). Pilot plant effluent samples were taken every 30 min during loading and analyzed for U. Eluate samples were taken every 2 min during the early stages of elution and every 30 min later. Selectively interdispersed samples were also analyzed for Fe, Al, Th, S.

The volume of the bioleach solution used to saturate the column varied depending on the bioleach solution composition.

Following uranium loading, the columns were drained and the biomaterial was washed with tap water in an up flow direction. After washing, the columns were drained again.

The biomass beds were then eluted with 25 l of 0.5 N $NaHCO_3$ solution prepared with distilled water in an up flow direction. Tap water had the following typical composition:

Ca: 18 mg/L,
S : 8 mg/L,

Mg: 2.2 mg/L,
Si: 2.1 mg/L,
Al: 0.1 mg/L.

The average eluant flow rate was 32.0 L/min (Standard deviation: 1.5 mL/min). Samples were taken during elution and analyzed for the elements mentioned previously.

During periods of interruption in feed water supply the pilot plant was maintained at a continuous low flow of acidified tap water. This proceedure was successful in avoiding problems of contaminating growth that were encountered during the operation of the previous pilot plant.

2.4 Analytical Methods

2.4.1 Uranium Analysis

Uranium (VI) analysis was carried out at CANMET by the fluorimetry technique. Examples of repeated uranium analysis of separate Denison Mines bioleach solution samples adjusted to pH 4.0 have been described in our previous report.

The standard deviation for the uranium analysis of the pilot plant feed ranged between 4% and 10%. The standard deviation of the uranium analysis for the eluate which contained uranyl carbonate complexes was better than 12%. Thorium was analysed by HPLC (High Pressure Liquid Chromatography). For Th and S, the highest standard deviation calculated was 2% from the analysis of 3 samples repeated 5 times.

Fe, Ca, Mg, Si, Al were analysed by the ICP (Inductively Coupled Plasma) method. The standard deviation was better than 5%.

3. RESULTS AND DISCUSSION

3.1 Uranium Sequestering Results

3.1.1 Uranium Loading

In the course of the previous pilot plant testing it was realised that aluminum and iron were the elements that were responsible for the observed reduction in the biomass uranium uptake capacity. The incorporated pretreatment could potentially eliminate these problems.

Uranium was selectively removed with 100% efficiency from the mine solution in all cycles. The uranium uptake breakthrough curves were similar to those experienced and reported for the previous pilot plant that was operated one year earlier. The biosorptive breakthrough curves showed a consistent narrow biosorption zone suggesting favourable kinetic properties for the immobilized biomass particles. The feed solution uranium concentration was not constant among the various shipments of mine water. Figures 2 to 4 illustrate the effluent uranium concentrations that were monitored for column PB as well as reactors R1 and R2.

The data on Figures 2 to 4 suggest that the reduction in the uranium uptake capacity was observed in the same way as in the previous pilot plant work. The incorporated pretreatment achieved a substantial reduction in iron feed concentration and a minor reduction in aluminum concentration but that was not sufficient to eliminate the aluminum competition to uranium biosorption. The average uranium uptake capacity of the biomass in R1 was low because of the accumulation of competing ions during the previous pilot plant experiments during which it had been used. The use of reactor R1 did not benefit reactor R2 with respect to the interference on uranium uptake by the competing ions.

3.1.2 Uranium Elution

Uranium elution was complete and efficient in all elution cycles irrespective of eluant flow rate. Figures 5 to 7 summarize the observed uranium elution for the first 3 cycles for R2. The eluate uranium concentration profile was always narrow and exhibited a tailing which was the result of the mixing zone that was establised in the upper third of the reactor R2 during elution because of carbon dioxide evolution. This tail was not experienced in the previous pilot plant work. Its origin was the hydraulic behaviour of the biomass bed during elution as explained above. The volume of eluant required to elute the adsorbed uranium can be further optimized so that the uranium concentration of the eluate, as well as its purity, can be increased further. It is possible to recover the entire adsorbed uranium in a small fraction of the presently used eluant thus producing uranium eluate concentrations perhaps four times higher than those presently observed. With the presently employed elution practice, a peak eluate uranium concentration of up to 7.8 g/L was observed.

3.2 Behaviour of Other Elements

The monitoring of the behaviour of the other elements listed in earlier sections of the present report led to several interesting conclusions. The behaviour of the most significant elements is discussed in the following section.

3.2.1 Aluminum

The data from Figures 2 to 4 suggest that the immobilized microbial biomass of R1 was substantially equilibrated to the aluminum feed solution concentration thus aluminum broke through the pretreatment steps and R1 very early. The biomass

aluminum accumulation was low as experienced in the previous pilot p[lant work. Figure 5 illustrates typical aluminum breakthrough curves observed in cycle 3.

The aluminum elution behaviour was the same as the one experienced in the previous pilot plant. During elution only part of the adsorbed aluminum was eluted. The important characteristic of aluminum elution was that it eluted partly and very early during the elution part of each cycle requiring only a very limited volume of eluant.

3.2.2 Iron

The low iron concentration that passed through the pretreatment stage was adsorbed by the immobilized microbial biomass particles of the first reactor. The behaviour of iron was predictable and has been discussed by Tsezos et al in detail in the literature and in the previous pilot plant study report. The high adsorptivity of the iron hydrolysis species and the upflow mode of column operation can explain these results.

During elution, iron was not eluted from the biomass as experienced in the previous pilot plant. As expected, elution of iron with the sodium bicarbonate solution (at an alkaline pH) was not observed. The low levels of iron in the feed solution are not considered responsible for the observed reduction in biomass biosorptive uptake capacity.

3.2.3 Thorium

Thorium has been shown in literature to accumulate in the microbial biomass. The detailed mechanistic study of thorium biosorption by Tsezos et al has suggested that the thorium biosorption site is different than that of uranium and that it is preferentially biosorbed at the outside of the fungal cell wall. Thorium biosorption behaviour in this pilot plant was similar to that of the previous pilot plant study and suggests that thorium was removed completely by adsorption

from the feed solution.

During elution and under the implemented elution conditions, thorium was eluted partially and at a later time than uranium as shown on Figures 6 and 7. This difference in elution behaviour confirms the previously identified opportunity for the separation of thorium from uranium which eluates earlier from the immobilized biomass biosorption column.

CONCLUSIONS

The results from the present work lead to the following conclusions:

1. The supplied immobilized biomass particles retain their physical integrity and characteristics for extended periods of use (exceeding one year).
2. The supplied immobilized biomass particles retain their favourable kinetic (rate) properties for extended periods of use (exceeding one year).
3. The immobilized biomass particles can efficiently and selectively extract and quantitatively recover uranium from dilute complex solutions.
4. The immobilized biomass particles uranium uptake capacity is affected during the first few cycles by the presence of aluminum and iron. Subsequently the uranium uptake capacity decreases very slowly.
5. Thorium also competes with uranium and reduces the uranium uptake capacity.
6. Adsorbed aluminum, thorium and uranium can be separated during elution as they elute at different times.
7. This biosorptive technology is characterised by high selectivity and could provide answers to
   (i) Radioactive waste water treatment
   (ii) Extraction and recovery of elements such as uranium and thorium.

9. The procedure that is available to eliminate the aluminum competion effects ,if so desired, is to remove the aluminum from the feed by a physical-chemical process following the suggested physical pretreatment of the feed. Alternatively, the biomass can be utilised, at a somewhat reduced capacity, in the presence of aluminum following only a physical pretreatment of the feed solution as suggested.

FIGURE 1

Flow sheet schematic of the pilot plant

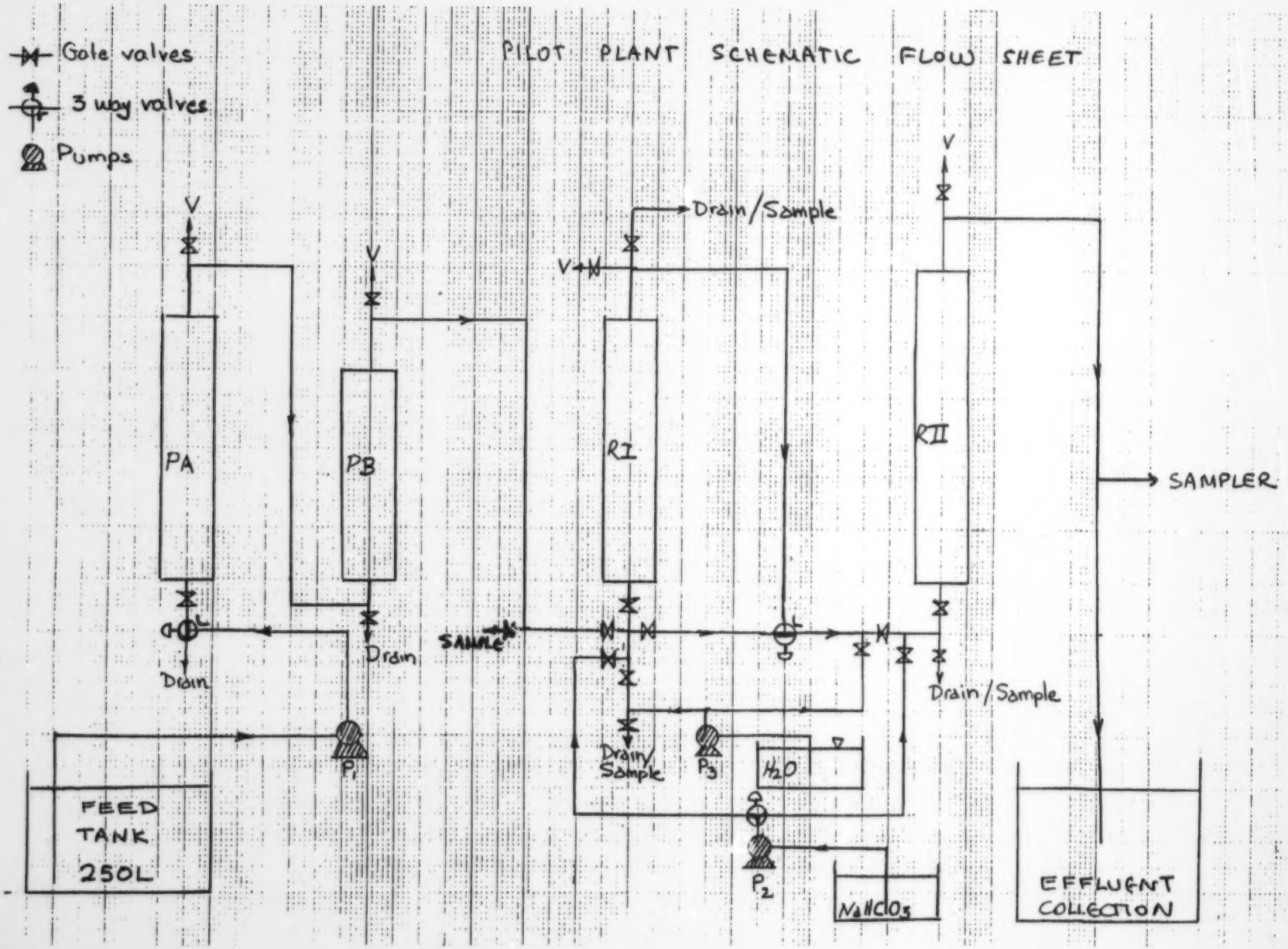
Gate valves
3 way valves
Pumps
PILOT PLANT SCHEMATIC FLOW SHEET
V
PA
PB
RI
RII
Drain/Sample
SAMPLER
Drain
SAMPLE
Drain/Sample
P1
P3
H2O
P2
NaHCO3
FEED TANK 250L
EFFLUENT COLLECTION

FIGURE 2

Uranium breakthrough curves for Cycle 1.
R1 designated as column B, R2 designated as column C

LOADING BREAKTHROUGH CURVE
CYCLE 1

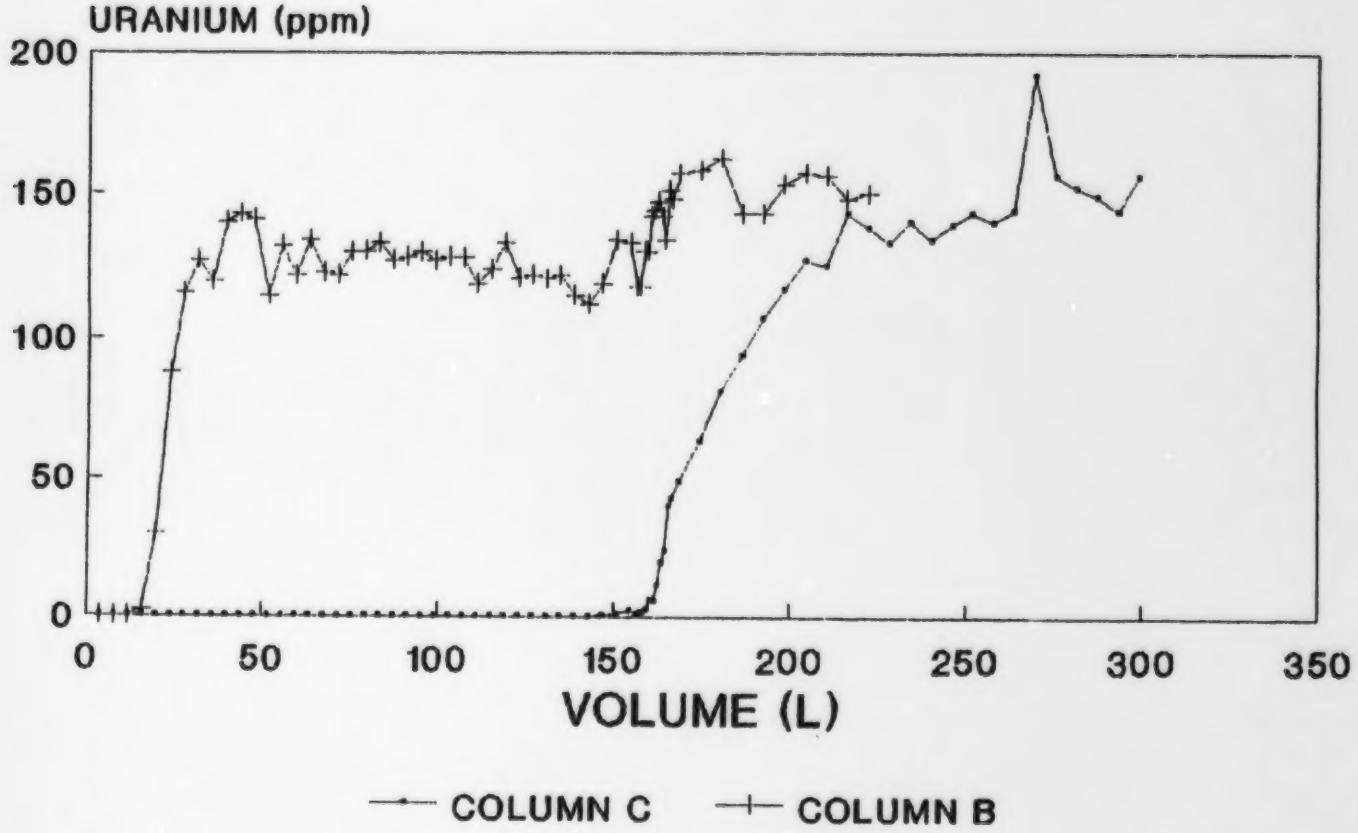

FIGURE 3

Uranium breakthrough curves for Cycle 2.
PB designated as column A, R1 as column B and R2 as column C

URANIUM LOADING
CYCLE 2

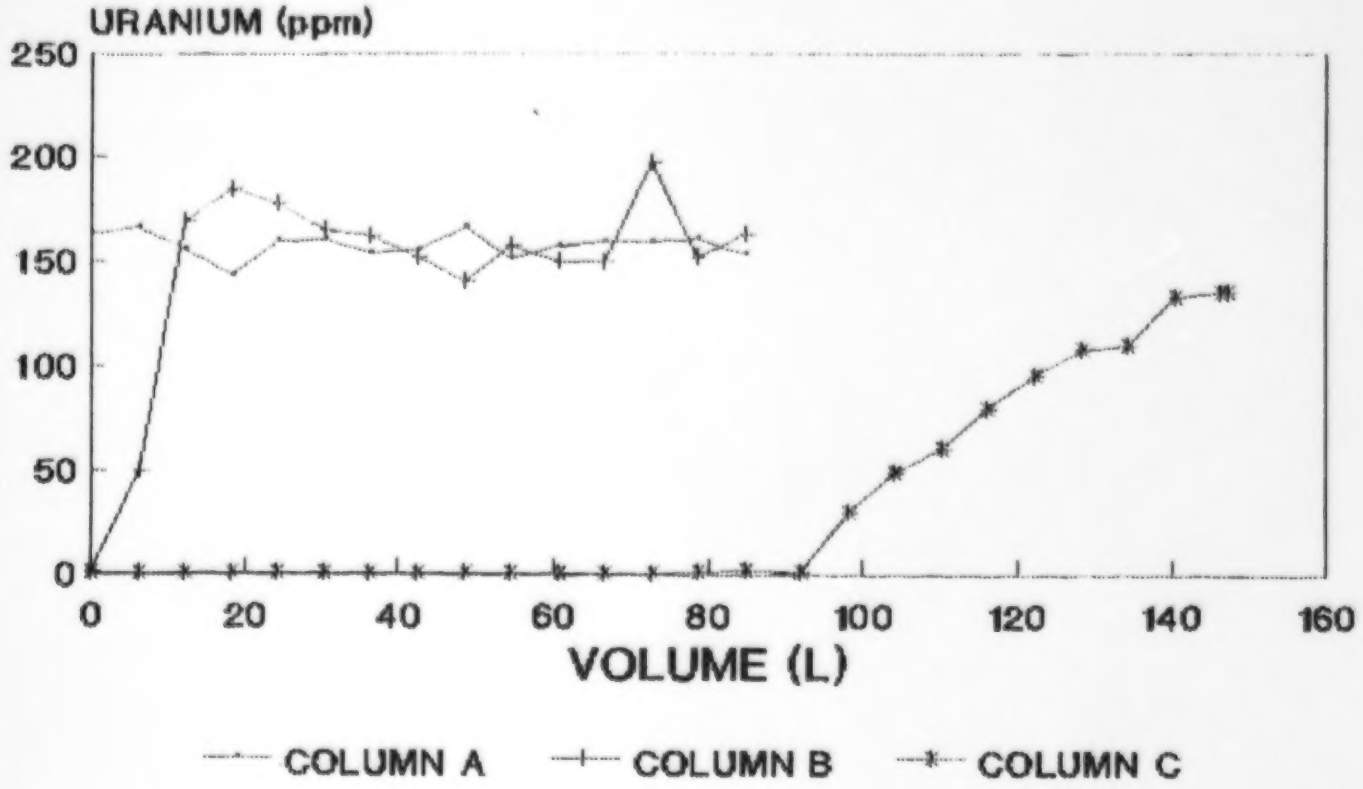

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FIGURE 4

Uranium breakthrough curves for Cycle 3.
PB designated as column A, R1 as column B and R2 as column C

URANIUM LOADING
CYCLE 3

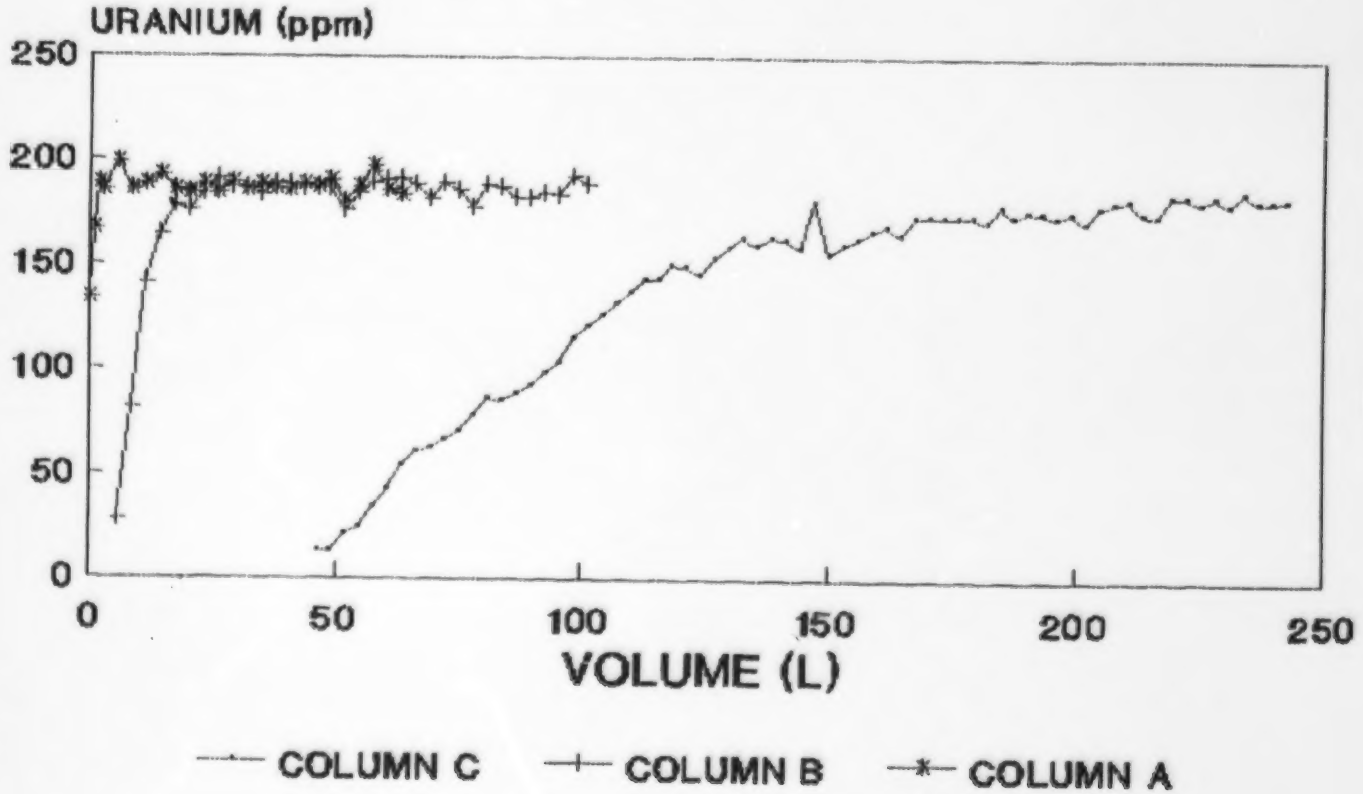

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FIGURE 5

Uranium elution curve for Cycle 1, reactor R2.

URANIUM ELUTION
CYCLE 1

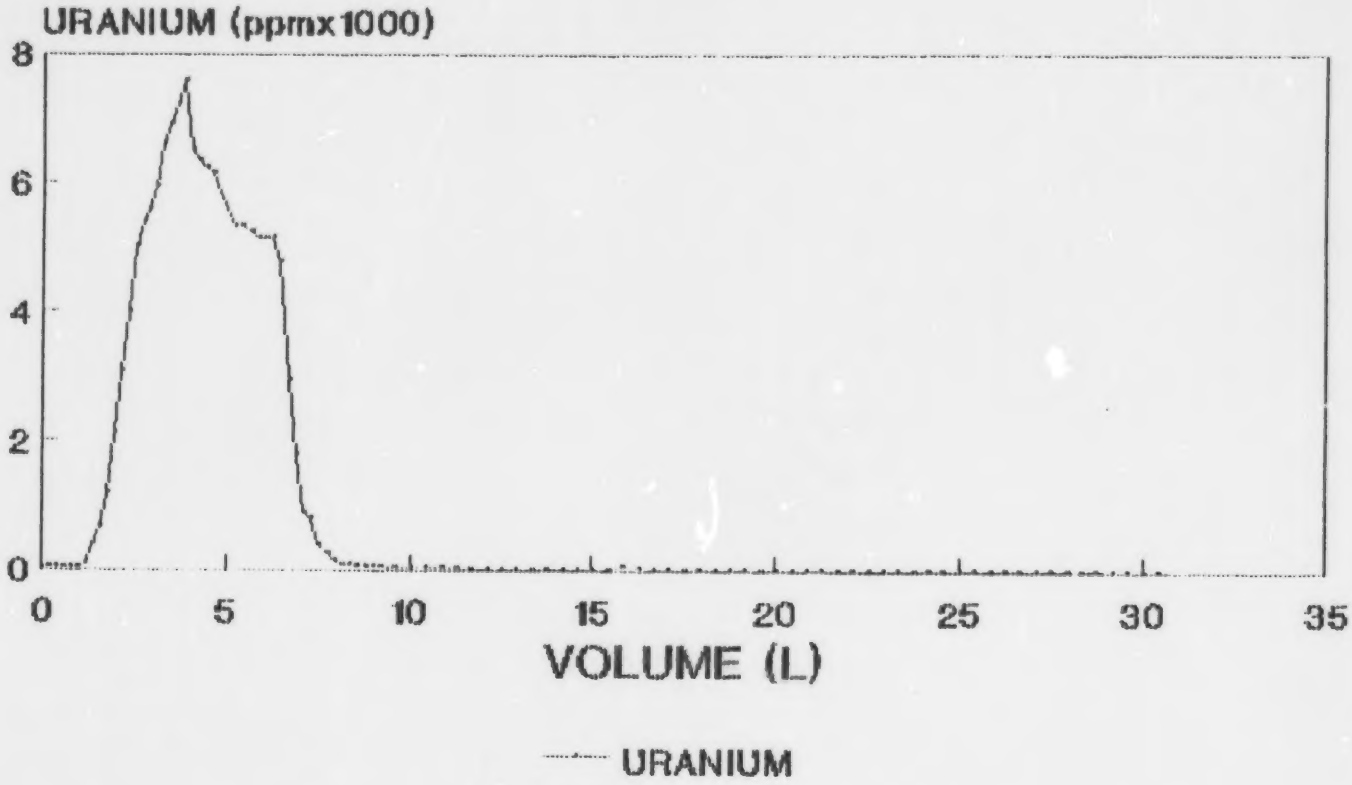

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FIGURE 6

Uranium elution curve for Cycle 2, reactor R2.

URANIUM ELUTION
CYCLE 2

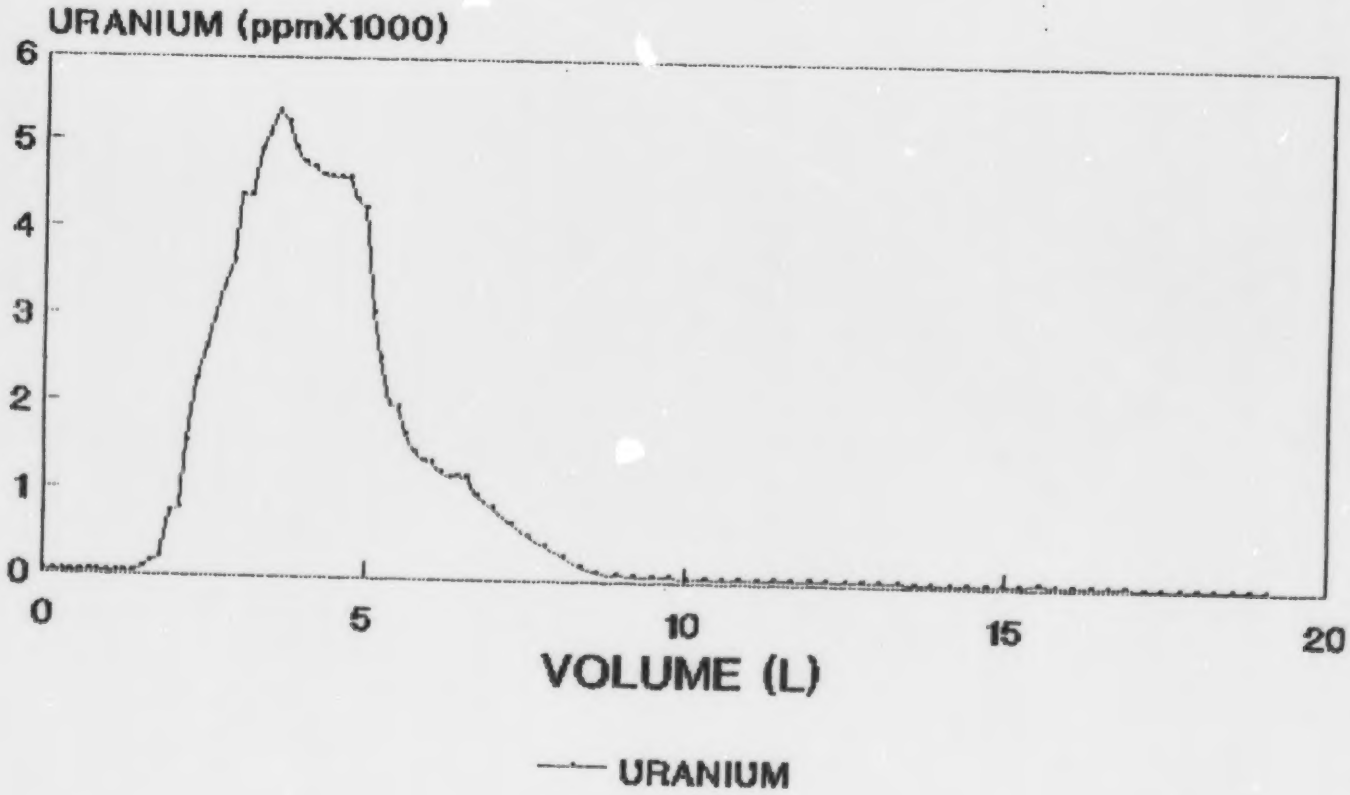

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FIGURE 7

Uranium elution curve for Cycle 3, reactor R2.

URANIUM ELUTION
CYCLE 3

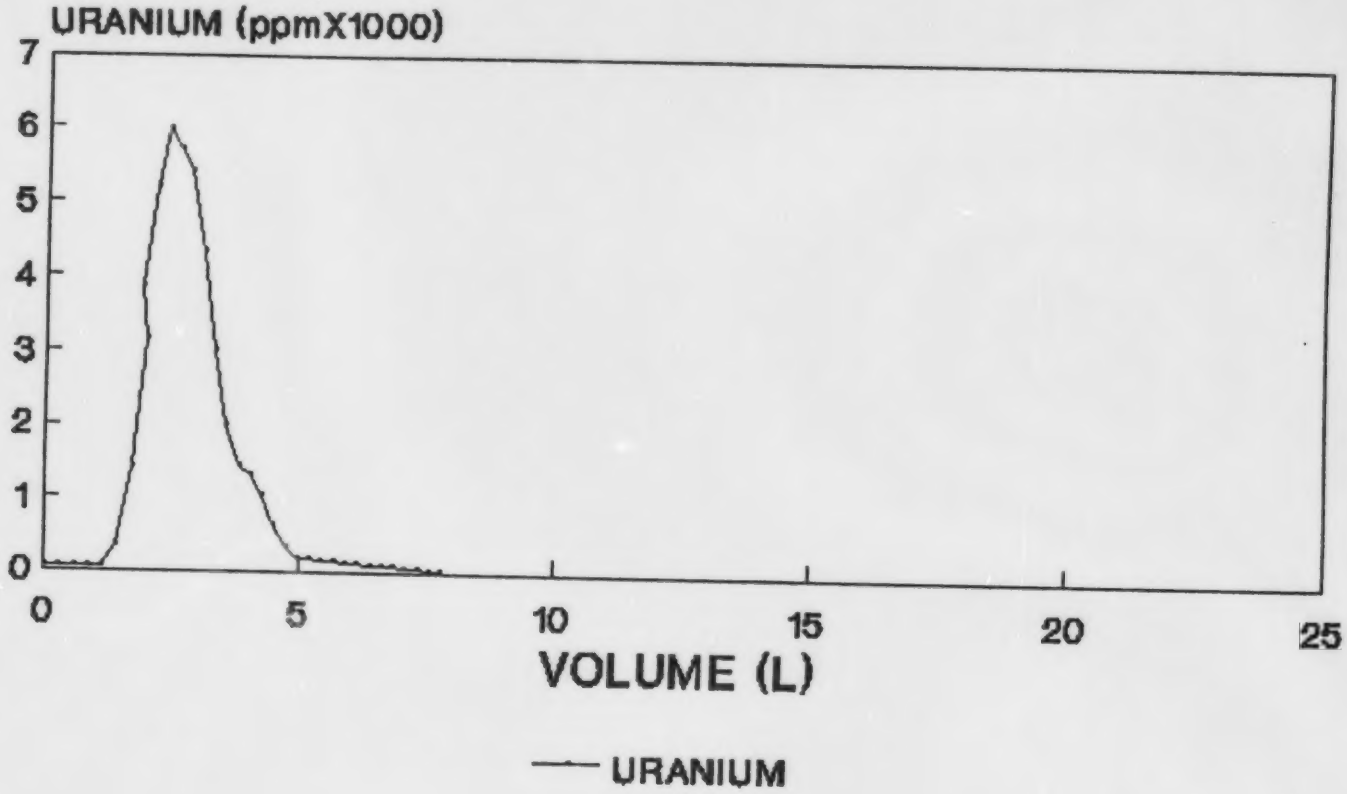

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FIGURE 8

Thorium elution curve from Cycle 1 ,reactor R2.

ELUTION
CYCLE 1

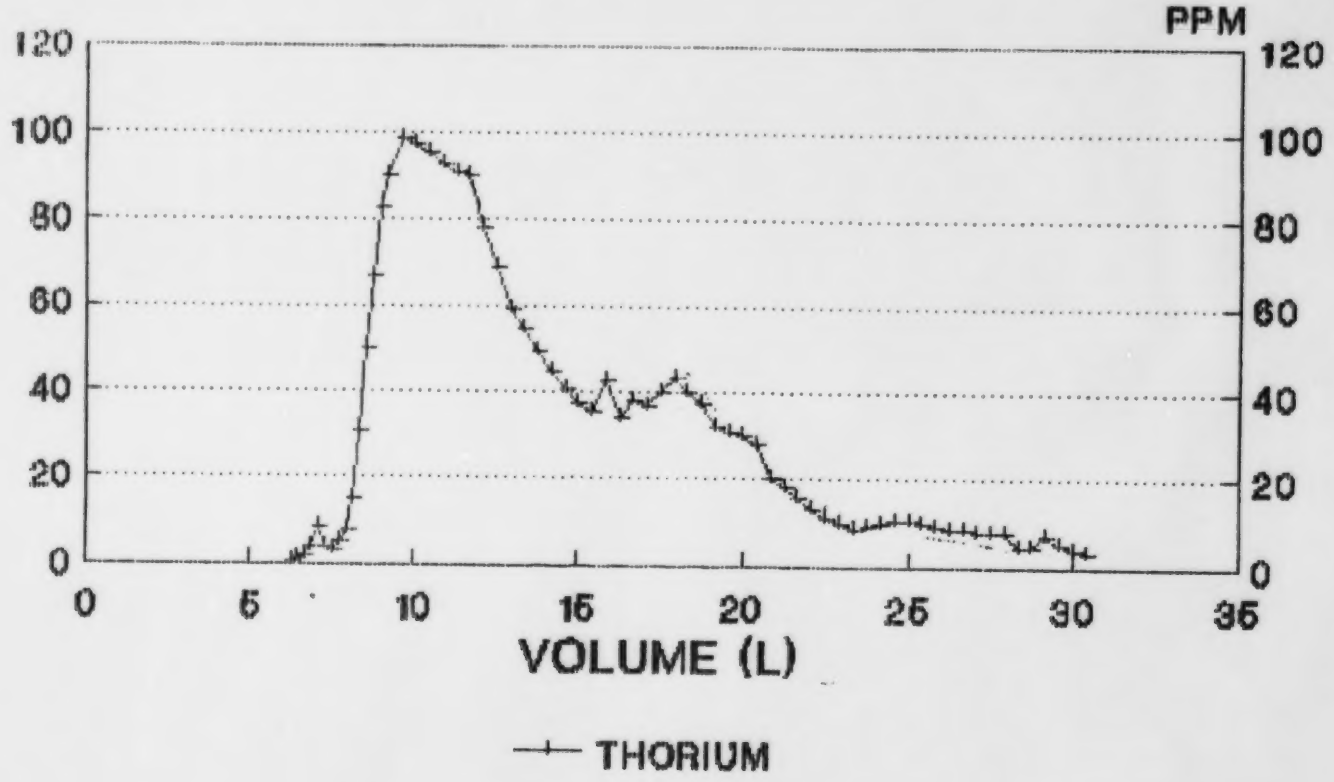

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FIGURE 9

Sulphur (sulphates) elution curve for Cycle 1, reactor R2.

ELUTION
CYCLE 1

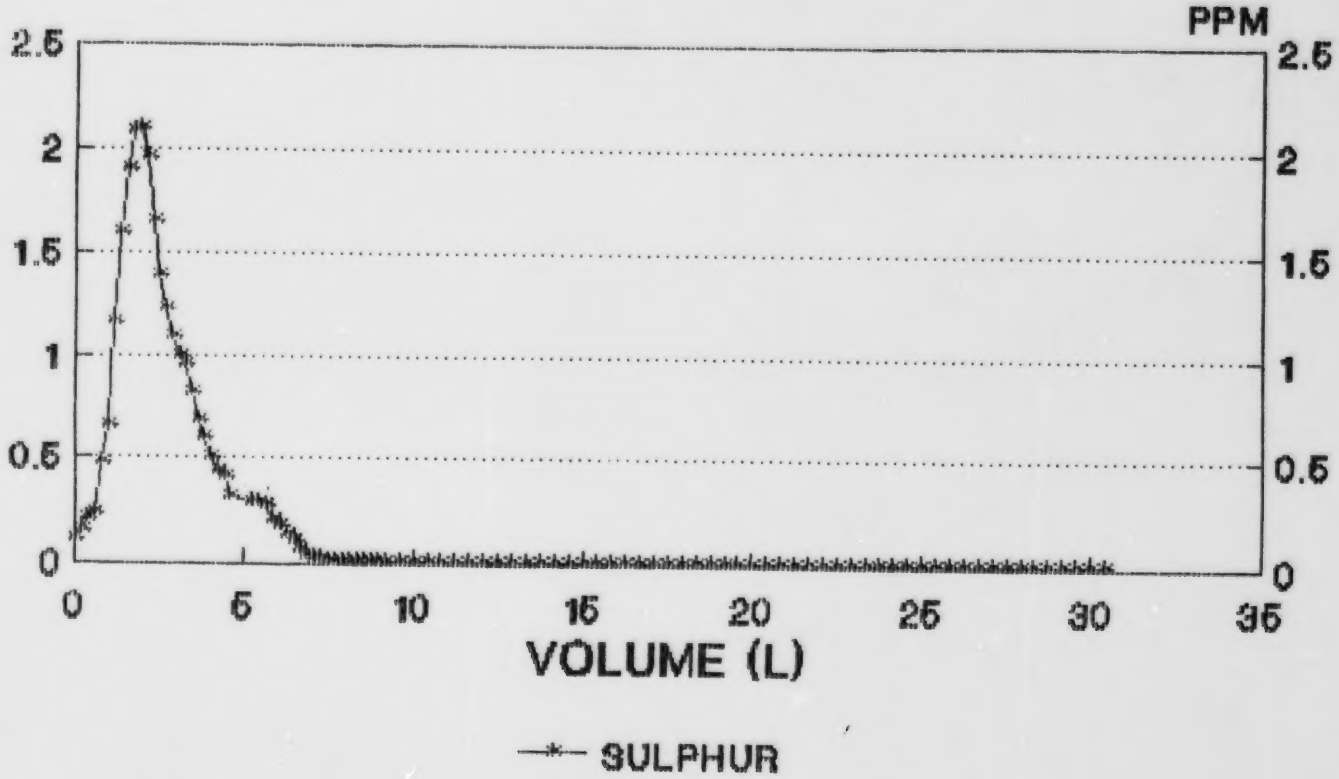

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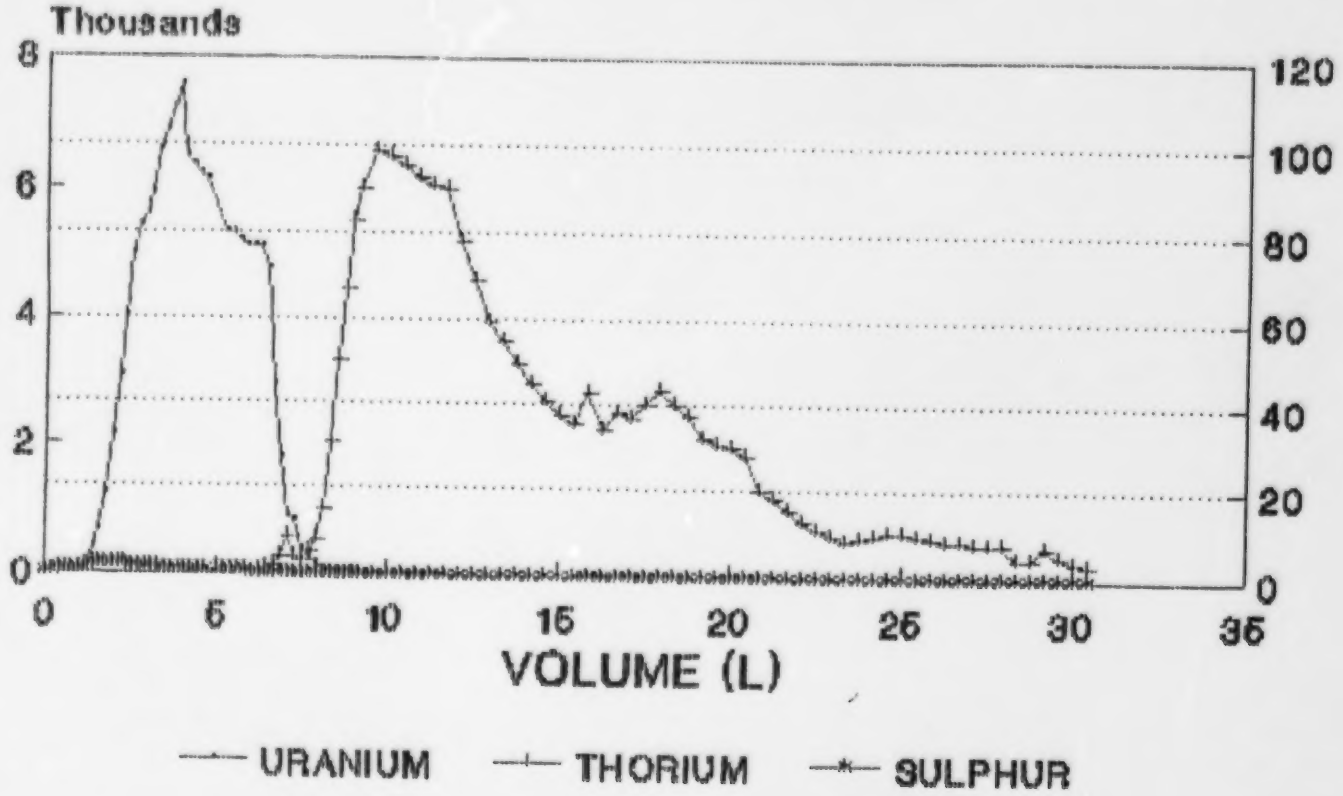
FIGURE 10

Comparison of elution behaviour of U, Th and S (sulphates) for Cycle 1, reactor R2.

ELUTION
CYCLE 1



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